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THE CHARACTERISTICS OF A LOW TEMPERATURE IN SITU SHALE OIL

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ABSTRACT

A 40° A.P.I. crude shale oil has been produced from the Green River Formation in the Piceance Creek Basin of Colorado by injection of hot natural gas at a controlled temperature. The quality of the shale oil differs very markedly from the customary shale oil from the same formation produced in a high temperature retort. The characteristics of the oil fractions have now been determined. These include distillation analyses, viscosity, and pour point determination.

Kinetic data on the production of the shale oil under the conditions used in the field, but carried out on a small scale in the laboratory, will be presented. A possible mechanism for the production of this oil, as well as a mechanism for the production of shale oil by more usual high temperature methods, is included.

TEXT

Various methods for the production of shale oil by in situ techniques are being investigated in the United States. The method with which this paper is concerned involves the use of hot natural gas as the energy conveying medium to convert the kerogen in the oil shale to a petroleum-like liquid. The basic concept, which was developed by the late J. L. Dougan of Equity Oil Company and tested in the Fuels Engineering Department laboratories at the University of Utah and subsequently field tested in the Piceance Creek Basin of Colorado, is basically a low temperature conversion and distillation process.[1] Natural gas is heated to a temperature below its thermal decomposition temperature and injected through an insulated pipe into the Green River Oil Shale formation where it loses its heat rapidly to the oil shale, gradually raising the temperature of the shale toward that of the injected gas. The kerogen is converted to bitumen and finally to a low pour point, high gravity crude oil.

Since the temperature of the natural gas is below that for thermal decomposition of the mineral carbonates in the oil shale, little CO_2 is produced.

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The natural gas is compatible with the oil, being soluble in it; this aids in the penetration of the formation by the natural gas and in the heat transfer. Since the heating gas is completely free from oxygen, no oxidation induced polymerization of the oil occurs.

Prior to the field experiment, oil shale cores from the Piceance Creek Basin were heated in a natural gas stream under two conditions. Some experiments were run at a gas pressure of 300 lb/sq inch. Experiments were also run with the gas at atmospheric pressure. In both cases it was demonstrated that the natural gas did, in fact, heat the oil shale to kerogen decomposition temperature and did convey the oil produced out of the retort and into condenser systems. Because of the large volume of gas used as a heating agent, the light ends of the produced shale oil were present at such low partial pressures that they were not condensed in the system available in the laboratory. The product was a waxy crude oil.

Subsequent experiments were carried out in non-flow systems or in systems using minimal amounts of natural gas or helium as a conveying agent. In these instances, yields of shale oil approaching 80 percent of the Fischer Assay yield of shale oil from the same cores, were obtained. Typical product evolution curves are shown in figure 1. In each case a relatively rapid, first

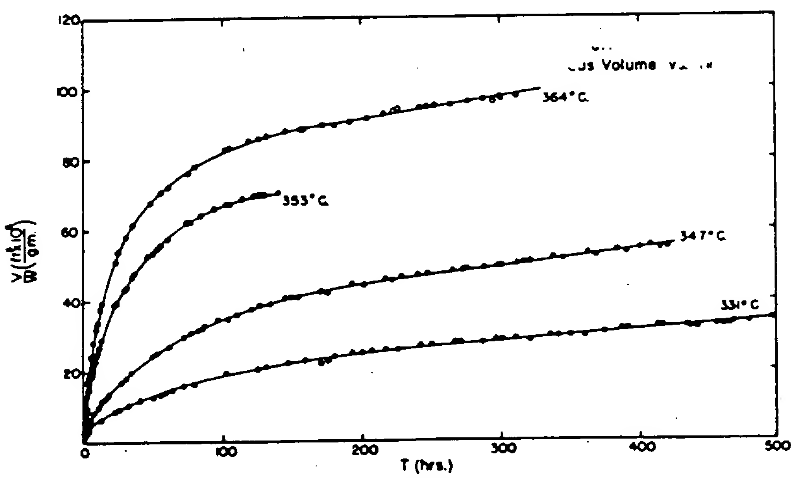

FIGURE 1.—Shale Oil Decomposition Isotherms.

order kerogen decomposition occurred followed by a zero order decomposition. Products continued to be evolved at a constant rate until finally almost all of the kerogen decomposable at that temperature had been evolved. The total distillate from these experiments had a pour point in the range of −20°C

and had an A.P.I. gravity of about 40°. The nitrogen content of the low temperature shale oil was less than 0.8 percent. Table 1 gives typical data on product yield and quality.

Since this shale oil differed so markedly from the shale oil produced by high temperature retorting methods, a careful analysis was made of kinetic studies on the production of bitumen and shale oil and gas recorded in the literature as well as of our experiments.

Based on these studies it has been concluded that two different mechanisms are possible for the production of shale oil from kerogen. These are indicated in equations (1) and (2).

$$\text{Kerogen} \xrightarrow{k_1} \text{Bitumen} \xrightarrow[T < 800°F]{k_2} \text{Oil} + \text{Gas} + \text{Residue} \qquad (1)$$

$$\text{Kerogen} \xrightarrow{k_1} \text{Bitumen} \xrightarrow[T > 800°F]{k_3} \text{Polymer} \xrightarrow{k_4} \text{Oil}' + \text{Gas}' + \text{Residue} \qquad (2)$$

Equation (1) involves rate constant k_1 for the conversion of kerogen to bitumen and rate constant k_2 for the production of oil, gas and residue from the bitumen, and is the path followed below 800°F. (426.7°C)

Equation (2) describes the "high temperature reaction." This involves the production of a polymer, rate constant k_3, from the bitumen or from the primary oil from reaction step k_1. This polymer then decomposes thermally by step k_4 into a different type of oil plus gas and residue.

In the low temperature process kerogen is converted to an organic soluble bitumen in a first order reaction with an activation energy of between 40 and 41.7 kilocalories. This step was delineated by Zimmerley[2] in a temperature range of 525°-690°F, and By Hubbard and Robinson[3] at the Bureau of Mines in temperature range 750°-890°F.

If the temperature remains low, i.e., below 800°F, the bitumen decomposes to give a paraffin-like oil with a rate constant k_2 the temperature dependence of which gives an activation energy in the range 42.5 to 48.5 kcal. The data used for evaluating rate contant k_2 and the activation energies were those of Hubbard and Robinson,[3] of DiRicco and Barrick,[4] and of Cane.[5]

If the sample of oil shale is heated to temperatures from 840°-1150°F which is a requirement if the oil is to be produced rapidly (as it must be in a retorting operation), the kerogen and initial oil are produced more rapidly than they can escape from the pores and matrix elements in which they are located. During the time of their confinement, they undergo many intermolecular collisions and polymerize to give thermo-dynamically more stable

products. As the heating is continued the polymer decomposes to give higher molecular weight products on the average than the primary oil. Typical high temperature retort oils have pour points of 80°F and A.P.I. gravities of 20°F.

The reaction with rate constant k_3 has an activation energy slightly higher than that of the reaction rate constant k_2. We estimate this to be in the range of 48-50 kcal. The activation energy for this step is not determinable directly, however, due to the fact that when this path is followed mechanical diffusion of the oil from the pores in the oil shale becomes rate determining. The data of Hubbard and Robinson[3] at high temperatures and of Allred and Nielsen[6] have been used to evaluate the activation energy for the diffusion controlled slow step and it ranges, depending upon the experimental technique used, between 13 and 25 kcal. These data and other data from which activation energies in other temperature ranges were calculated are in table 2.

In the high temperature processes all of the kerogen undergoes decomposition. The nitrogen atoms become an integral part of the polymer and the thermal decomposition of this polymer gives products containing this nitrogen well distributed among the final product molecules.

Based on the experimental results we have concluded that the nitrogen in the kerogen is present in molecules of very high molecular weight which tend to remain in the shale at the decomposition temperatures below 800°F.

To test the polymerization mechanism concept, samples of primary distillate from runs at 750°F were heated to 930°F in closed vessels for periods of 0.5 to three hours. In each instance extensive polymerization occurred.

Subsequent to the laboratory experiments in which the high gravity, low pour point, low nitrogen crude oil was produced, the Equity Oil Company conducted a field experiment in the Piceance Creek Basin of Colorado. In this experiment several holes were drilled into the Green River oil shale. Hot natural gas was injected through a central hole and the gas was returned through the peripheral holes in the matrix. The natural gas was reheated and recycled. The observed variations in recycle efficiency are being studied. Following a period of injection which was sufficient to heat a section of the formation to the kerogen decomposition temperature, shale oil from the formation was collected in a separator on the site. Samples were brought to the Fuels Engineering Department laboratory at the University of Utah for testing and other samples were submitted to the Atlantic Richfield Company for evaluation as a petroleum refinery feed stock. (Data-Table 2-16)

The oil from the field experiment was found to be essentially identical with that produced in non-flow tests at comparable temperatures in the laboratory experiments.

In figure 2 we have a distillation curve for the field shale oil sample and for a typical gas combustion retort shale oil sample. Figure 3 is a G. L. C. temperature programmed chromatogram of the oil. Table 3 gives the pertinent information on the fractions collected from the atmospheric pressure distillation of the oil. Additional properties of the distillate are shown in tables 4 and 5.

Tables 6 and 7 give analyses of the light ends from propylene through the C_6 family. Table 8 gives the paraffin hydrocarbon analysis of the fractions. In table 9 are tested olefin hydrocarbons. Table 10 gives data on various alkylbenzenes, indans, and naphthalenes.

In table 11 are listed the product distribution for the furnace oil and gas oil fraction of the light oil.

In order to determine the suitability of the shale oil as an oil refinery feed stock, cuts one and two have been blended, debutanized, and hydrotreated

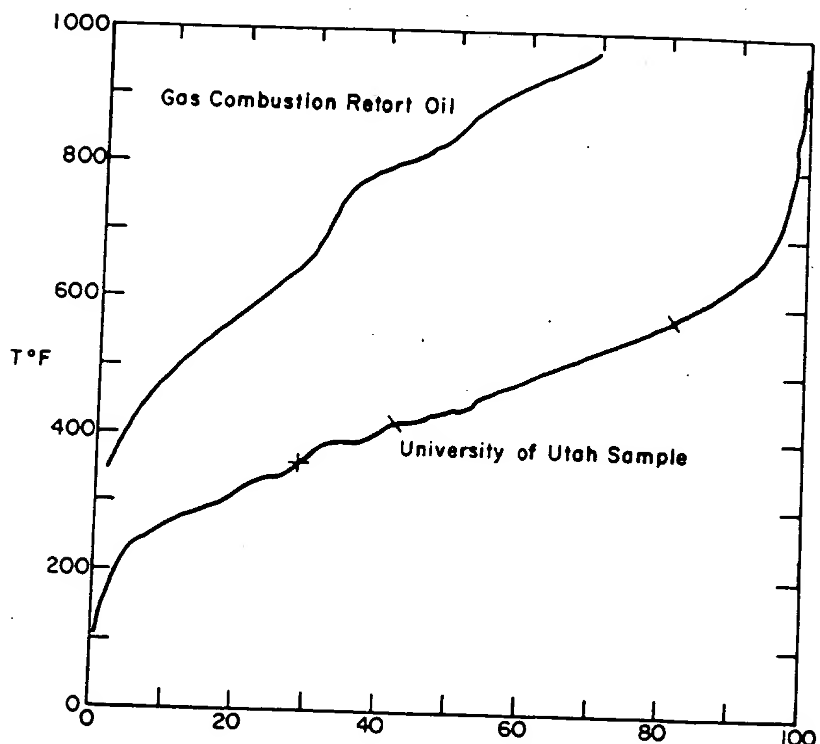

FIGURE 2.—Shale Oil Distillation Curves.

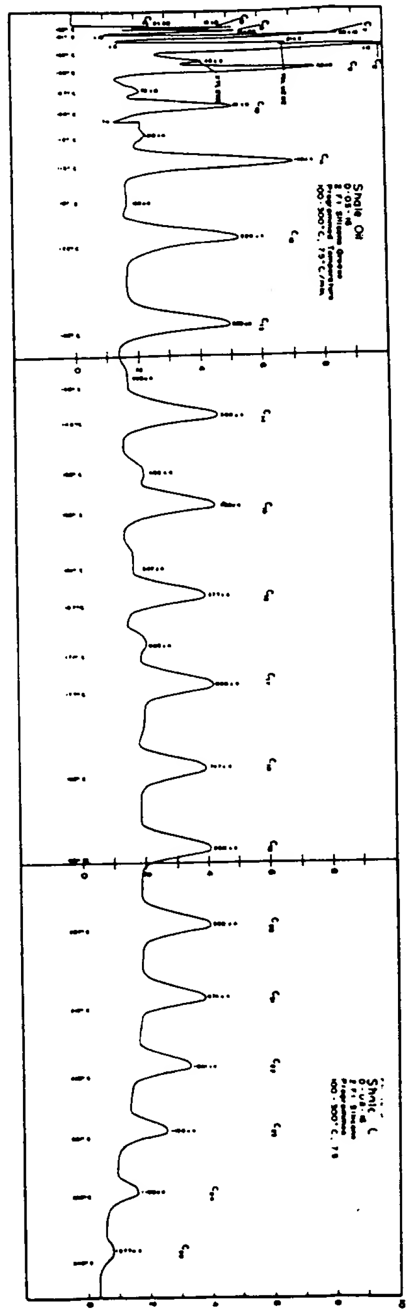

FIGURE 3.—Programmed Temperature Chromatogram of Shale Oil.

for olefin saturation and sulphur and nitrogen removal—all by calculation. In table 12 are given the data for the resulting pretreated reformer stock. This pretreated reformer stock has been fed into a reforming correlation using 350 lb/sq inch pressure; 7-1 hydrogen to hydrocarbon ratio; weight space velocity of 2; with Rd 150 catalyst. The results are given in table 13.

Table 14 gives the yield data from intermediate processing as percent of charge in a fluidized catalytic cracking unit. Table 15 is an evaluation of finished products from the standard catalytic cracking evaluation test of Atlantic Richfield. Table 16 completes the data from the laboratory catalytic cracking of Equity shale oil. Two conditions were used for each oil.

We conclude from these data that this oil should be hydrotreated prior to being cracked.

The ultimate analyses of three shale oil fractions are given in table 17.

SHALE RESIDUE

Microscopic examination of the shale residue following distillation unconfined and distillation of sample confined at 300 lbs/sq inch pressure show interesting results.

As the kerogen decomposes and volatilizes, voids appear to be left in the otherwise unaltered rock. These voids provide an interconnecting network and an internal porosity in the previously impermeable shale. The data in table 18 are new results from oil shale retorted under confining pressure. The final line in the table gives the data for the oil shale prior to treatment. These results confirm the important findings of Thomas[7] of Sinclair Oil.

The porosity introduced corresponds very closely to the volume occupied by the kerogen prior to its conversion to oil. Undoubtedly the porosity and permeability introduced into the shale will be important in continued production of oil from the formation.

TABLE 1.—*Effect of temperature on oil, yield and quality*

Temp. °F	*Time (hours)*	*Oil yield % of F.A.*	*Oil gravity °API*	*Pour point °F*
628	550	33.6	40.7	−40°
657	425	40.4	40.5	−49
667	159	39.1	39.4	− 9.4
687	312	52.6	41.6	− 0.4
743	71.0	71.6	37.4	− 4.0
750	88.5	72.8	39.4	− 9.4
788	38.0	72.8	38.6	− 4.0
801	37.5	78.1	27.7	+23
801*	14.7	72.9	42.3	− 7.6

*1000 p.s.i.

TABLE 2.—*Energies of decomposition of oil shale kerogen*

Author	*R*	*R. D. Step*	*T Range °C*	E_a
Zimmerley	B	(k_1)	275-365*	41.7
Hubbard & Robinson (U)	B	(k_1)	400-475	40.0
Hubbard & Robinson (U)	O+G	(k_2)	350-450 (52.6g/t)	46.2
Hubbard & Robinson	O+G	(k_2)	400-450 (26.7g/t)	42.4
DiRicco & Barrick	O+G+B	(k_1, k_2)	250-465	45.5
Cane	O+G+B	(k_2)	350-400	48.5
Hubbard & Robinson (A)*	O+G	(k_2)	429-477	40.5
Hubbard & Robinson (U)	O+G	(k_2, k_3, k_4)	450-525 (52.6g/t)	27.0
Hubbard & Robinson (U)	O+G	(k_3, k_4)	475-525 (26.7g/t)	19.0
Allred and Nielson*	O+G	(k_3, k_4)	477-531	25.8
Allred and Nielson*	O+G	(k_4)	531-616	13.6
This research	G		331-427	27.0
Hubbard & Robinson (U)	G		400-525	22.0

*$\ln\left(\frac{1-R}{R}\right) = -kt$; others are all $\ln(1-R) = -kt$ where $R = \frac{x}{\text{kerogen}}$

(U) Calculated at Univ. of Utah from data in reference.

...d and quality

...ity	Pour point °F
	−40°
	−49
	− 9.4
	− 0.4
	− 4.0
	− 9.4
	− 4.0
	+23
	− 7.6

...ale kerogen

T Range °C	E_a
...5-365°	41.7
...0-475	40.0
...0-450 (52.6g/t)	46.2
...0-450 (26.7g/t)	42.4
...0-465	45.5
...0-400	48.5
...9-477	40.5
...0-525 (52.6g/t)	27.0
...5-525 (26.7g/t)	19.0
...7-531	25.8
...1-616	13.6
...1-427	27.0
...0-525	22.0

... = x / kerogen

TABLE 3.—*Equity shale oil distillate cut properties*

Cut	Over-180°F	180-360°F	360-420°F	420-580°F	580°+F
Crude Range Volume %	0.5-2.5[1]	2.5-28.9	28.9-42.0	42.0-81.0	81.0-100
Crude Yield Volume %	2.0	26.4	13.1	39.0	19.0
Gravity-°API	73.7	52.9	43.8	36.6	30.3
Percent Sulfur	0.13	0.40	0.36	0.70	
Percent Nitrogen	0.01	0.16	0.37	0.36	
Research Octane 0 cc	[2]	42.5	38.9	—	
3 cc		56.9	51.4	—	

[1] 0.5 percent H_2O and gas
[2] Octane on blends of cuts 1, 2 and 3 = 40.0

TABLE 4.—*Equity shale oil distillate cut properties*

	0-360°F	360°-580°F	580°-995°F	955°+
Yield on Crude, Vol. Percent	28.5	52.4	18.4	0.7
°API	54.2	38.2	30.9	0.4
Sulfur, Wt. Percent	—	0.61	0.75	(High)
Nitrogen, Wt. Percent (Total)	—	0.36	0.75	—
CFRR, Oa Tel	40.5	—	—	—
Rams. Carb. Res.	—	0.13	0.17	—
Viscosity			299 SSU @ 275°F 1900 SSU @ 210°F 65000 SSU @ 122°F	
RI at 67°C	—	—	1.47050	—
RI at 80°C	—	1.4635	—	—
Pour, °F	—	-15	60	—
Bromine #	—	17	10.7	—

TABLE 5.—*Equity shale oil distillate cut properties*

Distillation	0-360°*F*	360°-580°*F* *atm*	580°-955°*F* 10 *mm*
IBP		400	290
5		413	334
10		420	340
20		430	352
30		438	362
40		448	372
50	265	459	382
60		471	394
70		486	408
80		503	428
90	325	525	460
95		541	492
EP		564	530
Rec.		98	91

TABLE 6.—*Equity shale oil analysis*

Cut	*Over*-180°*F*
Propylene	0.1
Propane	0.4
AV Butylenes	0.1
i Butane	1.0
n Butane	4.2
Pentanes	2.0
i Pentane	5.7
n Pentane	11.7
Cyclopentane	
	Light Ends by POD

Paraffins
C6
C7
C8
C9
C10
C11
C12

Cut
MCP
Monoolefin
DCP
CODA
TCP
Cydiolefins

TABLE 7.—*Equity shale oil analysis*

	0-360°*F*
iC_4, Vol. Percent	0.1
nC_4, Vol. Percent	0.3
C_5's Vol. Percent	1.3
C_6 + P, Vol. Percent	63.4
C_6 + N, Vol. Percent	25.1
C_6 + A, Vol. Percent	9.8
C_6 + Mol Wt.	124

TABLE 8.—*Equity shale oil analysis*

Paraffins	*Over*-180°*F*	180-360°*F*	360-420°*F*
C6	35.9	1.5	0.7
C7	15.1	7.6	0.5
C8		15.2	0.6
C9		19.2	0.8
C10		14.4	10.6
C11		2.9	33.2
C12			14.1

TABLE 9.—*Equity shale oil analysis*

Cut	*Over*-180°*F*	180-360°*F*	360-420°*F*
MCP	15.1	18.5	16.4
Monoolefin	3.6	3.3	2.3
DCP	0.1	1.5	0.2
CODA	1.3	2.6	
TCP			0.7
Cydiolefins	0.1	2.6	4.9

TABLE 10.—*Equity shale oil analysis*

Cut	*Over-180°F*	180-360°*F*	360-420°*F*
Alkylbenzene			
C6	3.1	0.3	0.1
C7	0.5	1.8	0.5
C8		3.1	0.9
C9		3.6	2.1
C10		1.0	3.9
C11		0.1	2.5
C12			0.5
Indans		0.3	3.6
Napthalene		0.4	0.9

TABLE 11.—*Equity shale oil analysis*

	Furnace Oil 360-580°*F*	*Gas Oil* 580-955°*F*
Volume % Crude	42.1	19.0
Analysis		
Normal Paraffin	31.5	0.8
Isoparaffin	13.8	38.3
Mono and non-condensed Cycloparaffin	18.8	15.3
Polycycloparaffins		2.3
Olefins	4.6	5.1
Mono Aromatics	25.0	21.6
Naphthalenes	5.6	8.5
Phenanthrenes	0.7	6.0
Benzanthrenes + 5 ringers		1.0
Chrysenes and Pyrene		1.1
Total Arom.	31.3	38.2
Mono Ar. in total percent	80.0	56.5
NP + IP	49.9	44.2

360-420°F
0.1
0.5
0.9
2.1
3.9
2.5
0.5
3.6
0.9

Gas Oil 580-955°F
19.0
0.8
38.3
15.3
2.3
5.1
21.6
8.5
6.0
1.0
1.1
38.2
56.5
44.2

TABLE 12.—*Equity shale oil pretreated reformer stock*
(Blends of Cuts 1 and 2)

	Volume Percent
C_5's	1.3
C_6 + Paraffin	63.8
Napthalenes	25.1
Aromatics	9.8
54.2° API	
50 Percent at 285°F	
90 Percent at 325°F	
40.5 Clear Octane	

TABLE 13.—*Reformer product qualities (calculated)*

C_5+*F-1 0 cc*	85 *Wt*	85 *Vol*	90 *Wt*	90 *Vol*	95 *Wt*	95 *Vol*
H_2	1.5		1.6		1.7	
C_1	1.1		1.5		1.8	
C_2	1.8		2.4		3.2	
C_3	2.5	3.7	3.0	4.5	3.6	5.4
C_4	*2.4*	3.2	*2.9*	3.8	*3.4*	4.5
C_4	9.3		11.4		13.7	
C_5+ API	47.1=.7923		45.3=.8003		43.1=.8104	
C_5+	90.7	87.2	88.6	84.4	86.3	81.1
C_5's in C_5+	5.6		6.9		8.5	
C_5+RVP	2.5		2.8		3.3	
F-1 3 cc	95.5		98.4		101.2(W)	
F-2 0 cc	77.4		80.7		84.0	
F-2 3 cc	86.8		89.2		91.5	
St. Temp.	910		923		938	
BBL/# Lives-First Cycle	36		20		11	
BBL/# Lives-Ult.	150		85		45	

TABLE 14.—*Intermediate processing yields as percent of charge Equity shale oil*

Process	*Reforming*	*853 FCCU Cracking (Pace)*	
Charge stock	*Reformer stk.*	*"Normal" gas oil (taking virgin F.O.M. "as such")*	*"Long" gas oil (includes virgin F.O.M.)*
" Cut pts.	0-360°F	580-955°F	360-955°F
" % Crude	28.54	18.55	70.95
Products			
Hydrogen (SCF/B)	614.6	—	—
Therms/Bbl.	2.21	4.06	1.50
Propane	5.34	3.75	3.45
Propylene	—	5.00	3.00
n-Butane	2.89	1.50	1.95
i-Butane	1.78	3.15	4.65
Butylene	—	.95	1.60
Gaso. Comp (C5+)	84.85	46.30	43.60
F.O.M.	—	33.70	41.10
Gaso. Comp. Properties			
RON—0	85.00	91.91	80.92
RON—3	95.23	97.65	87.20
MON—0	77.93	82.38	75.07
MON—3	88.09	87.48	80.01
RVP	3.26	4.37	4.62

TABLE 15.—*Standard catalytic cracking evaluation-finished products Equity shale oil*

	Virg. FOM as FOM	*Virg. FOM to GO*
Reg. Gasoline, B/B of Crude	.384	.660
FOM, "	.588	.291
Plant Fuel, "	.030	.029
#6 Fuel, "	−.023	−.023
Propane, "	.022	.038
n-Butane, "	−.031	−.038
Hydrogen, MCF/B	(.25)	(.23)
Gas, Therms/B	(3.6)	(5.0)
Gas and Loss	.030	.043
Total	1.000	1.000

TABLE 16.—*Laboratory catalytic cracking of Equity shale oil*

	360-580°F	*Furnace oil*	580-955°F	*Gas oil*
430°F Conversion—				
Vol. Percent	21.6	29.7	26.6	38.3
Wt. Percent coke	3.4	4.4	5.7	7.7
Wt. Percent C_3 and lighter	2.1	3.8	3.5	5.1
Vol. Percent C_4's	2.9	5.5	4.6	7.0
Vol. Percent C_5 to 430°F	40.4	39.5	16.3	22.5

TABLE 17.—*Equity shale oil fractions ultimate analysis*

Fraction	*S*	*O*	*C*	*H*	*N*	*Carbon Residue*
Gasoline (<354°F)	0.52	0.64	85.4	14.1	0.5	0.1
Kerosene (354-473°F)	0.72	0.75	83.6	13.3	0.8	1.3
Residue >473°F	0.67	0.55	86.2	12.8	1.1	2.0

TABLE 18.—*Retorted oil shale under confining pressure*

Time Above 650°F Hours	*Retort Temp. °F*	*Volume Change %*	*Weight Loss %*	*Induced Porosity*	*Induced Permeability*	
					Plug Md.	*Whole Core Md.*
48	805	+3.2	15.32	28.4	0.3	46
48	799	+1.9	16.28	26.8	0.1	128
40	800	+2.7	15.38	27.6	0.1	197*
0	75	0	0	0.8	0.0	0

*Cleavage parted core completely

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